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Applicant(s): Chai-Jing Chou; Eddy I. Garcia-Meitin

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NANOCOMPOSITE

This invention relates to polymers reinforced with delaminated or exfoliated multi-layered silicates, that is, nanocomposite polymers.

Nanocomposite polymers are compositions comprising a relatively high number (but relatively low weight) of preferably single layers of exfoliated silicate material dispersed in a given volume of continuous polymer matrix, see United States Patent 5,717,000 to Seema V. Karande, Chai-Jing Chou, Jitka H. Solc and Kyung W. Suh, United States Patent Application Serial Number 034,620 filed December 31, 1996 and Giannelis, "Polymer Layered Silicate Nanocomposites", Advanced Materials, 1996, 8, No. 1, pages 29-35. As discussed in the '000 patent and as is well known in the art, nanocomposite polymers exhibit many increased physical property enhancements at a much lower weight percent of filler than conventionally filled polymers. Other patent literature disclosing nanocomposites include United States Patents 4,810,734, 4,558,075 and 3,516,959; as well as WO 93 04117 A and EP-A-0 459 472. Edge coating of multi-layer silicate material is known, see United States Patents 4,434,075 and 4,964,918.

However, it can be difficult to get the multi-layer silicate material to exfoliate into the polymer.

The instant invention is a solution, at least in part, to the above stated problem. In one embodiment, the instant invention is a process for producing a nanocomposite polymer by dispersing a multi-layered silicate material into a thermoplastic polymer. The process comprises the step of mixing a quaternary ammonium intercalated multi-layered silicate material with the thermoplastic polymer at a temperature greater than the melting or softening point of the thermoplastic polymer, characterized by the quaternary ammonium intercalated multi-layered silicate material having been reacted with a polyvalent anionic organic material so that the edges of the multi-layered silicate material are bound to the polyvalent anionic organic material to form a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material.

The instant invention in another embodiment is a process for producing a nanocomposite polymer by dispersing a multi-layered silicate material into a thermoset polymer. The process of this embodiment comprises the steps of: (a) mixing a quaternary ammonium intercalated multi-layered silicate material with a thermoset prepolymer, characterized by the quaternary ammonium intercalated multi-layered silicate material having been reacted with a polyvalent anionic organic material so that the edges of the multi-layered silicate material are bound to the polyvalent anionic organic material to form a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material; and (b) curing the thermoset prepolymer to set the thermoset polymer.

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The instant invention in yet another embodiment is a composition comprising: (a) a polymer; and (b) a multi-layered silicate material dispersed in the polymer, the multi-layered silicate material having edges, characterized by at least a portion of the edges of the multi-layered silicate material being bound to a polyvalent anionic organic material.

5 The instant invention in further yet another embodiment is process for

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producing a nanocomposite polymer, comprising the steps of: (a) mixing a quaternary ammonium intercalated multi-layered silicate material with a monomer, characterized by the quaternary ammonium intercalated multi-layered silicate material having been reacted with a polyvalent anionic organic material so that the edges of the multi-layered silicate material are bound to the polyvalent anionic organic material to form a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material; and (b) polymerizing the monomer.

Montmorillonite clay (a multi-layered silicate material) is stirred in water with an excess of 3,400 molecular weight sodium polyacrylate (a polyvalent anionic copolymer of mole ratio 1:1 of ethylene and acrylic acid) available from the Rhone-Poulenc Company to edge treat the clay. The edge treated clay is then stirred with an excess of a mixed quaternary ammonium compound (68 percent bis hydroxyethyl, dodecyl, methyl-quaternary ammonium compound and 32 percent bis hydroxy C-6 to C-9, dodecyl, methyl-quaternary ammonium compound) to produce a polyacrylate edge coated quaternary ammonium intercalated montmorillonite. The polyacrylate edge coated quaternary ammonium intercalated montmorillonite is washed with water and dried. Ninety five parts of ethylene adipate thermoplastic polyurethane (available from The Dow Chemical Company) is melted (or softened) in a polymer mixer at 160 degrees Celsius at 200 rpm. Five parts of the dried polyacrylate edge coated quaternary ammonium intercalated montmorillonite, as described above in this paragraph, is added to the mixer and mixed for five minutes. Transmission light microscopic examination of the product shows significantly fewer one hundred micrometer sized clay clusters relative to the use of non-edge coated material. Transmission electron microscopic examination of the product shows single and multiple layer exfoliation of the silicate layers of the montmorillonite. The layers are counted in a representative view. Most preferably, more of the layers are present as single layers than are present as multiple layers. In any event the dispersion of the layers into the polymer is improved using the instant invention relative to the use of a non-edge-coated material.

Polyvalent anionic organic materials are organic chemicals that have more than one carboxylic acid or other anionic substituant such as a sulfonate or a phosphonate. Preferably, the polyvalent anionic organic material is a polyvalent anionic polymer. Most preferably, the polyvalent anionic organic material is polyacrylic acid. However, the specific polyvalent anionic organic material used in the instant invention is not critical and can include, without limitation thereto, for example, copolymers of styrene and acrylic acid or styrene and sulfoethylmethacrylate.

The above referred to '000 patent and the '620 patent application list exemplary multi-layered silicate materials required in the instant invention. For example, the multi-layered silicate material can be, without limitation thereto: montmorillonite; nontronite; beidellite; volkonskoite; hectorite saponite; sauconite; magadiite; medmontite; kenyaite;

laponite, mica, fluoromica and vermiculite. The above referred to '000 patent and '620 patent application also lists exemplary onium or quaternary ammonium compounds required in the instant invention. For example, the onium compound can be, without limitation thereto, quaternary ammonium compounds having octadecyl, hexadecyl, tetradecyl or dodecyl moieties. However, the specific multi-layered silicate material or onium compound used in the instant invention is not critical.

However, it should be understood that it is preferable to use polar substituted quaternary ammonium compounds with relatively polar polymers such as nylons and polyurethanes. Similarly, it is preferable to use non-polar substituted quaternary ammonium compounds with relatively non-polar polymers such as polypropylene and polyethylene. The terms "polar" and "non-polar" are used in their conventional sense. For example, a polar substituted quaternary ammonium compound is a quaternary ammonium compound having a hydroxy ethyl (C₂OH) or hydroxy hexyl (C₆OH) substituent(s).

The selection of a preferred quaternary ammonium compound is aided by comparing the electron photomicrographs of the nanocomposites made using the quaternary ammonium compounds being tested in the instant invention to determine which quaternary ammonium compound(s) give the greatest degree of exfoliation of the multi-layered silicate. Of course, physical property improvement of the nanocomposite v. the base polymer is the final objective of the instant invention but such improvement is often a function of the degree of exfoliation of the multi-layered silicate.

In addition to mixing the polyvalent anionic organic quaternary ammonium intercalated multi-layered silicate material with a molten thermoplastic polymer, the instant invention also includes mixing the polyvalent anionic organic quaternary ammonium intercalated multi-layered silicate material with a monomer(s) or thermoset prepolymer(s) followed by the polymerization of the monomer(s)/prepolymer(s). Examples of thermoplastic polymers include, without limitation thereto, polypropylene, polyethylene, polystyrene, polystyrene copolymers, acrylic polymers, acetyl polymers, thermoplastic elastomers, urethane, epoxy, polyester, nylon, polycarbonate, and blends thereof. Examples of thermoset polymers include, without limitation thereto, epoxy, phenolic, urethane, rubber, and blends thereof.